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Formation of Volatile Organic Compounds (VOC's) During Pulping

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Abstract

This study measured the concentration profiles of major water soluble volatile organic compounds (VOC's), i.e., methanol, acetone, and methyl ethyl ketone (MEK), during conventional pulping processes of southern pine, birch, and kenaf in a laboratory digester. These VOC species were mainly formed at early stage of the cooking. The study shows that more methanol is formed in kraft pulping than in soda pulping. The study also verifies the conclusion in the literature that hardwood pulping will produce more methanol than softwood. Kinetic analysis indicates that the overall methanol formation reaction follows Arrhenius kinetics well. The catalyst, anthraquinone, increased the methanol formation in softwood kraft pulping, but reduced methanol formation in kraft hardwood pulping.

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INTRODUCTION

The formation of volatile organic compounds (VOC's), such as methanol and methyl ethyl ketone (MEK), during kraft pulping processes has been an environmental concern. These VOC's are soluble in water and become an important source of biodegradable organic compounds to increase the biochemical oxygen demand (BOD). Furthermore, these species can also be released into the atmosphere at the process temperatures of kraft mill streams. With the increasingly restrictive environmental regulations such as the cluster rule [1], many VOC's are now on the list of hazardous air pollutants (HAP's) that are required to be controlled. The knowledge on VOC formation during the pulping process is limited. The quantity of VOC formed (VOC yield) during pulping was not reported in the literature. The effects of pulping conditions and catalyst on the VOC yield during pulping have not been studied. Therefore, research on VOC yield during various pulping conditions using different raw materials can provide useful information to estimate the VOC formation in pulp mills. The knowledge gained can help to develop technologies to reduce VOC emission at its source, i.e., during pulping.

Methanol has been identified as the main alcohol in pulp mill process streams [2-4]. A list of various VOC's present in pulp mill streams was summarized by Bethge and Ehrenborg [5] and Blackwell et al. [6]. According to Clayton [7], methanol could be formed by the rapid alkaline hydrolysis reaction of 4-O-methylglucuronic acid residues in hemicellulose (or demethylation of xylan). Although methanol can also be formed through the hydrolysis of methoxyl groups in lignin (demethylation of lignin) [6, 8], the amount of methoxyl groups that can be demethylated is very small [8]. Therefore, it is reasonable to assume that the majority of methanol is formed through the demethylation of xylan [7, 8]. Wilson and Hrutfiord [2] conducted a study on the reaction mechanism of VOC's using mill samples and analytical grade chemicals. They proposed that fermentation is the main formation pathway to all alcohol except methanol, and methyl ketones are formed by air oxidation of wood extractives followed by a reverse alcohol condensation. Later, Wilson et al. [9] studied the effect of wood species on the formation of VOC's in pulping and concluded that hardwood can yield many more VOC's than softwood.

The objective of the present work is to quantify VOC yields from different pulping processes using various raw materials. The concentrations of methanol, acetone, and methyl ethyl ketone (MEK) during each cooking process were obtained by analyzing the cooking liquor samples collected during various stages of pulping. The information obtained can be used to develop VOC formation model for the prediction of VOC release in pulp mills.

EXPERIMENTAL

The pulping experiments were carried out in a laboratory batch digester (ME&K). Conventional pulping processes were employed in this study. The load of each batch cooking was 800 grams of oven dried (O.D.) chips. Four types of raw materials were used in this study, i.e, southern pine (softwood), birch (hardwood), and kenaf bast and kenaf core (nonwood). Southern pine and birch were pulped separately by both kraft and soda processes, with and without a catalyst, anthraquinone (AQ). Kenaf bast and core were pulped separately using soda-AQ process only. The detailed pulping conditions are listed in Table I. After the addition of the chips and cooking liquor, temperature of the digester was raised from room temperature to 100°C in 20 minutes. Then it was brought to 170°C in an hour, and maintained at 170 °C for two hours. After the completion of the cooking, the digester was cooled to room temperature by draining the black liquor. The pulp was thoroughly washed before the handsheets made for kappa number and viscosity analysis. The final kappa numbers of fibers from all the cooking processes are listed in Table II.

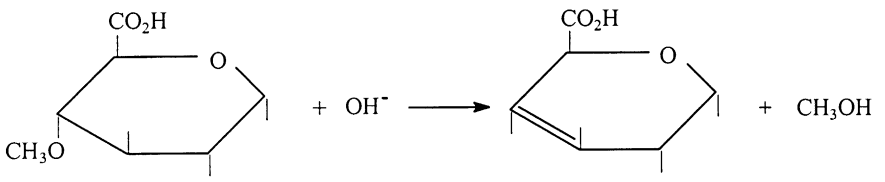
During each cooking process, a small amount (15 mL) of cooking liquor was collected at about 15- 20 minute intervals after the temperature reached 100°C. The concentrations of methanol, acetone, and methyl ethyl ketone (MEK) in the collected liquors were analyzed using an indirect headspace gas chromatographic method that we developed [4]. We also determined the absorption of dissolved lignin in cooking liquor by UV spectroscopy [10].

RESULTS AND DISCUSSIONS

The VOC's in the kraft mill condensate streams, especially these most quoted in the literature [5, 6], include alcohols, ketones, phenolics, terpenes, and organic sulfur compounds. The composition of VOC's formed during pulping is related to the wood species and the pulping process employed. For example, a very significant amount of α-pinene was formed during softwood cooking. For kraft pulping, it was found that dimethyl sulfide is a dominant malodorous organic compound remaining in the cooking liquors [4]. The amount of methyl mercaptan (MM) is not significant in the solution because of its low boiling point. Methanol, acetone, and MEK were the major water-soluble volatile organic compounds found in the cooking liquors from both kraft and soda pulping process. In this study we found that Methanol concentration in the cooking liquors could reach to 1000 mg/L. The amount of acetone and MEK were relatively low compared with methanol, about 2 to 8 mg/L in the cooking liquors. The other water-soluble volatile compounds, such as ethanol, were not significant in the black liquors.

Methanol Mass Balance

The purpose of chemical pulping is to separate fibers that consists of cellulose and hemicellulose by dissolving wood lignin in the cooking liquor through the so-called delignification process. During a pulping process, methanol can be formed mainly through the degradation of 4-O-methyl-D-Glucuronoxylans in hemicellulose through hydrolysis [7] as shown in reaction (1). According to Sarkanen et al. [8] methanol formation through the hydrolysis of the aromatic methoxyl groups in lignin structure can be neglected.



(1)

In this study, we measured the methanol concentrations in the cooking liquors collected at various stages of all the pulping experiments. Fig. 1 shows the methanol concentration and UV absorption of the dissolved lignin measured as function of cooking time in a kraft cooking of southern pine (softwood). The results show that the methanol concentration increased as temperature increased. It was found that the formation of methanol increased along with dissolved lignin during the first one and half hours of the pulping process. After that, the dissolved lignin concentration continued to increase, while the methanol content leveled off. This further confirms that lignin demethylation reaction is less significant and hemicellulose xylan degradation through hydrolysis reaction (1) is the dominant methanol formation mechanism during pulping processes. Reaction (1) was supported by xylan hydrolysis studies using model xylan compounds [7]. The methoxyl groups from the 4-O-methyl-glucuronoxylan was found close to zero after two hours of hydrolysis reactions [7]. We can carry out a mass balance calculation to estimate the methanol yield based on the assumptions of 100% conversion of methoxyl groups in xylan to methanol and negligible lignin demethylation. The amount of 4-O-methyl-glucuronic acid $m_{megacid}$ in per unit mass of wood chip can be expressed as the xylan content x_{xylan} divided by the ratio of xylose to the 4-O-methyl-glucuronic acid $R_{megacid}$,

$$m_{megacid} = \frac{x_{xylan}}{R_{megacid}}. \tag{2}$$

According to Eqn. (1), one mole of 4-O-methyl-glucuronic acid forms one mole of methanol. Therefore the amount of methanol formed per unit mass of wood chip will be:

$$m_{MeOH} = \frac{M_{MeOH}}{M_{megacid}} \cdot m_{megacid}, \tag{3}$$

where $M_{MeOH} = 31$ and $M_{megacid} = 186$ are the molecular weight of methanol and the 4-O-methyl-glucuronic acid in wood xylan, respectively. The methanol concentration (mg/L) in cooking liquor can be expressed as

$$[C_{MeOH}] = \frac{m_{MeOH}}{R_{LW} \cdot m_{wood}} \times 10^6 = \frac{M_{MeOH}}{M_{megacid}} \cdot \frac{x_{xylan}}{R_{LW} \cdot R_{megacid}} \times 10^6, \tag{4}$$

where R_{LW} is the liquor to wood mass ratio.

Table III lists the sample calculations of methanol concentration using eqn. (4) for the southern pine (softwood) and white birch (hardwood). The xylan content x_{xylan} and the ratio of xylose to the 4-O-methyl-glucuronic acid $R_{megacid}$ listed in the Table are based on the data given by Fengel and Wegener [11]. We found that methanol concentrations in the final cooking liquors of southern pine and birth are 1041 and 740 mg/L, respectively. We also listed the methanol concentrations (averaged over kraft, kraft-AQ, and soda-AQ processes) in the final cooking liquors measured in this study. The calculated methanol concentrations account for 78% and 73% of those measured in birch and pine liquors, respectively. The unaccounted methanol must be formed by the hydrolysis of methoxyl groups in lignin (lignin demethylation). According to Sarkanen et al. [8] wood lignin hydrolysis reaction consists of a rapid phase followed by a slower phase. Sarkanen et al. [8] studied various wood lignin hydrolysis reactions at a temperature range of 170-200°C with alkali concentration of 5-15%. Based on their experimental data, we assumed that the lignin methoxyl group hydrolyzed is 2% for birth to estimate the contribution of lignin demethylation to methanol formation in the pulping of birch and pine we conducted in this study. Because softwood lignin demethylation data are not available and softwood is usually hard to delignin, 1.5% is arbitrary assumed in estimation. The estimation procedure is similar to that of eqns. (2) - (4). The estimation also considered the fact that softwoods contain only coniferyl alcohol, while hardwoods contain both coniferyl (50-75%) and sinapyl alcohols (25-50%) [12]. Sinapyl alcohol contains two methoxyl groups while the coniferyl alcohol only has one as shown in Fig. 2. The calculation results shown in Table IV suggest that lignin demethylation only contributes less than 20% of the methanol formed in pulping. Table V lists the methanol mass balance based on the above calculations and the experimentally measured data. We found that only less than10% of the methanol were not accounted for, which could be due to very small amount of methanol formed by extractives and the measurement error that was about 5% [4].

Methanol Formation Reaction Rate

Since xylan demethylation contributes to about 80% of the methanol formed during pulping with the assumption of 100% methoxyl group conversion. We can use the rate of xylan

demethylation reaction (1) to represent the overall methanol formation reaction rate. We can use the following equation to express the rate of the reaction,

$$\frac{d[C_{MeOH}]}{dt} = -k'[C_{CH_3O^+}]\cdot[C_{OH^-}]. \qquad (5)$$

The hydroxyl concentration $[C_{OH}^-]$ is very large during the entire pulping process, therefore reaction (1) can be treated as first order. The methoxyl concentration is equal to its initial concentration minus the methanol concentration, i.e., $[C_{CH_3O^+}] = C^0_{CH_3O^+} - [C_{MeOH}]$,

$$\frac{d[C_{MeOH}]}{dt} = -k\left\{C^0_{CH_3O^+} - [C_{MeOH}]\right\}. \qquad (6)$$

Therefore, we can determine the methanol formation reaction rate k of a given pulping process as a function of temperature using the experimentally measured methanol concentration in this study. Fig. 1 shows the methanol concentration at various stages of a pulping experiment we conducted. To obtain an analytical solution for k, we used a Boltzmann function expressed in Eqn.(7) to fit the measured methanol concentration,

$$[C_{MeOH}] = C_T + \frac{C_0 - C_T}{1+\exp\left(\frac{t-t^*}{\Delta t}\right)}, \qquad (7)$$

where $C_T = 1000$ and $C_0 = 248$ mg/L are the final and the initial methanol concentration, t^*=71.4 and Δt=11.4 are two time parameters of the Boltzmann distribution. By taking the derivative vs time of Eqn. (7), we have,

$$\frac{d[C_{MeOH}]}{dt} = \frac{\exp\left(\frac{t-t^*}{\Delta t}\right)}{\left[1+\exp\left(\frac{t-t^*}{\Delta t}\right)\right]^2}\cdot(C_T - C_0)\Delta t = \frac{(C_T - [C_{MeOH}])([C_{MeOH}] - C_0)}{C_T - C_0}\cdot\Delta t \qquad (8)$$

Combining Eqns. (6) and (8), we have,

$$k = \frac{(C_T - [C_{MeOH}])([C_{MeOH}] - C_0)}{(C_T - C_0)(C^0_{CH_3O^+} - [C_{MeOH}])} \cdot \Delta t \qquad (9)$$

The initial methoxyl group concentration $C^0_{CH_3O^+}$ can be determined using the procedure discussed in the previous section. Since the methanol concentration is directly related to the pulping temperature. We can find the methanol formation reaction rate k as a function of temperature for the data presented in Fig.1. For consistency, we used the experimentally measured methanol concentration in the calculations. Furthermore, we assume $C^0_{CH_3O^+} = C_T$. We can also express the reaction rate k in the Arrhenius form as shown in Eqn. (10),

$$k = A \cdot \exp(-\frac{E_A}{RT}) \qquad (10)$$

We conducted a linear regression analysis for the calculated reaction rate k in a temperature range of 100–170°C as shown in Fig.3. We found that the natural logarithmic of k vs the inverse of temperature in Kelvin fits to a straight line very well, suggesting that the reaction follow the Arrhenius kinetics. From the regression results, we can obtain the reaction activation energy E_A = 81,189 J/mol and the kinetic pre-exponential factor A= 2.5887x10^{10}. We found that for all the pulping processes conducted in this study, the overall methanol formation reactions follow the Arrhenius kinetics.

We would like to point out that the above analysis is an empirical analysis with the assumption of homogeneous first order reaction. Clearly, the diffusion of hydroxyls in the cooking solution into wood chip is an important factor in the actual heterogeneous pulping reactions. Furthermore, large errors may occur in this type of analysis due to limited measurements taken during the temperature ramping period of the pulping process and the sampling and measurement uncertainties, therefore quantitative comparisons of the activation energies of methanol formation reactions among various pulping processes are not so

meaningful. However, the above estimation can provide qualitative information about the methanol formation during a pulping process.

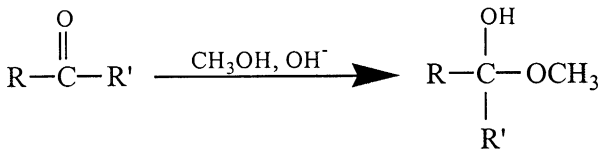
Comparisons between Softwood and Hardwood

Figs. 4 and 5 show the concentration profiles of VOC's during kraft and soda pulping of softwood and hardwood. We found that the methanol concentration profiles are almost the same for both using softwood and hardwood except that more methanol are produced in hardwood cooking than that in softwood cooking. More methanol formation was also reported by Wilson et al. [9]. Hardwood has a higher content of 4-O-methyl-D-glucuronoxylans in hemicellulose than softwood does and hardwood lignin has more methoxyl groups than softwood lignin does [12]. Softwoods contain only coniferyl alcohol, while hardwoods contain both coniferyl (50-75%) and sinapyl alcohols (25-50%). Sinapyl alcohol contains more methoxyl groups than coniferyl alcohol as shown in Fig. 2. Furthermore, the peak methanol formation rate in hardwood pulping is higher than that in softwood pulping. Ninety percent of the methanol was formed within the first 75 minutes in the hardwood pulping processes. It took about 90 minutes to achieve 90% of the methanol in softwood pulping.

Figs. 4a and 5a also indicate that kraft pulping always yields more methanol than soda pulping does for both hardwood and softwood used in this study. As mentioned above, alkaline hydrolysis as shown reaction (1) is the dominant methanol formation mechanism during most of a pulping process. In the kraft process, the presence of hydrogen sulfide ions can greatly facilitates delignification because of their superior nucleophilicity as compared with hydroxyl ions. Therefore more hemicellulose and dissolved lignin are released from wood chips in the kraft pulping process. As a result more methanol can be formed through the demethylation reactions of xylan and lignin.

According to Wilson and Hrutfiord [2], all of the ketones found in pulping, as methyl ketones, are formed through the air oxidation of extractives followed by decomposition of the extractive hydroperoxide, which undergoes a reverse alcohol condensation at a high temperature in the digester. We found in this study that the major ketone species generated in all the pulping processes were acetone and MEK. The concentration profiles of these ketones during the

pulping were quite different from those of methanol as show in Figs. 4b and 5b. The profiles of both acetone and MEK are similar in both the kraft and soda pulping of softwood, i.e., the contents of acetone and MEK reached a maximum at 50 minutes or close to the maximum cooking temperature and then decrease after temperature reached 170°C. This behavior could be explained as a result of hemiacetals, or hemiketals' reactions between methanol and ketones [13]. Either acetals or ketals can react with methanol to form hemiacetals or hemiketals under certain conditions as follows,



Aldehyde or ketone — Hemiacetal or hemiketal (11)

which leads to a decrease in ketone concentration as cooking continues. For certain unknown reasons, the acetone and MEK concentrations in the kraft hardwood pulping process did not decrease until very late in the cooking process as shown in Fig. 5b. Further study to understand this phenomenon is needed. Figs. 4b and 5b also show that more acetone than MEK is formed in both kraft and soda pulping of a hardwood and a softwood.

It was also found that further extending the cooking process beyond 3 hours can result in a decrease in methanol and ketones concentration, as shown in Figs. 4 and 5. The decrease in concentrations of methanol and ketones is probably related to condensation.

VOC Formation During Pulping of Kenaf

Fig. 6 shows the formation of methanol, acetone, and MEK in the soda-AQ pulping of kenaf bast and core. It was found that the cooking of kenaf core produced much more methanol than the cooking of bast. This is because that kenaf core has a much higher lignin content of about 17% than that of the bast about 7% [14]. The behaviors of ketone formation in the soda-AQ pulping of kenaf core are similar to those of kraft pulping of hardwood. The peak

concentrations of ketones in bast pulping were shifted to a later pulping time compared to those in the pulping of core.

Effect of Catalyst on VOC Formation

We conducted two sets of experiments to evaluate the effect of a catalyst, anthraquinone (AQ), on VOC formation during pulping. We found that the methanol concentrations were essentially identical for the first hour of all cooking processes studied as shown in Figs. 7 and 8. The significant differences in methanol formation with or without AQ is only at the later stage of the pulping processes when the cooking temperature is high (170°C). The catalyst increased the formation of methanol by 15% in softwood kraft pulping, as shown in Fig. 7, while an opposite phenomenon is observed in hardwood kraft pulping, i.e., the catalyst reduced the formation of methanol by about 10%, as shown in Fig. 8.

As discussed previously, methanol is formed through two mechanisms, i.e., degradation of xylans in the hemicellulose through the reaction of (1) and the demethylation of lignin. According to Wilson et al. [9], xylan degradation is the dominant methanol formation mechanism. As proposed by Clayton [7], xylan degradation in alkaline pulping of wood is brought about by the conversion of 4-O-methyl-D-glucuronic acid groups present in xylans into the corresponding unsaturated acids. This postulation was later verified by Johansson and Samuelson [15]. They found that a model compound of xylan, 2-O-(4-O-methyl-D-glucopyranosyluronic acid)-D-xylito7l can react with sodium hydroxide (1 M) at 150°C to yield 50% hexeneuronic acid after 90 min reaction time. The reaction also forms methanol at the same time. This indicates that xylans can be partially degraded and form methanol at a high pulping temperature. In pulping, the formation of methanol from xylans is mainly in the early stage of the cooking. Holton confirmed that the AQ possesses a marked capability of accelerating the delignification and leads to an increase in pulp yield [16]. On the otherhand, Lowendahl and Samuelson indicated that AQ has the ability to stabilize the polysaccharides such as xylan toward alkaline degradation [17]. Hardwood has a high content of xylan (15-30%) and a low content of lignin (18-25%) [12]. The effect of stabilization of xylans is probably significant enough to slow down the reaction (1) in an AQ pulping of hardwood, therefore less methanol is formed as shown in Fig. 8. Softwood has a low content of xylan (5-10%) and a high content of lignin (25-35%)

[12], therefore, delignification acceleration is perhaps more significant than the stabilization of xylan degradation by AQ to produce more methanol in softwood pulping.

SUMMARIES

This paper presents the concentration profiles of three major water-soluble, steam-volatile organic compounds, i.e., methanol, acetone, and MEK, during the conventional pulping processes. These compounds are mainly generated in the initial stage of the cook at temperature 170°C. More methanol can be produced in hardwood pulping processes than in softwood. Kraft pulping processes produce more methanol than soda processes. A methanol mass balance calculation based on 100% conversion of methoxyl groups in xylan indicate that hemicellulose degradation accounts for about 75% of the methanol formed in pulping. The demethylation of lignin only accounts for about 15% of the methanol formed based on a 2% lignin methoxyl group conversion given in the literature. Kinetic analysis indicates that the overall methanol formation reaction follows Arrhenius kinetics well. The formation behaviors of acetone and MEK in the processes are different from that of methanol. These ketones have probably undergone a hemiacetal or hemiketal reaction with methanol in most pulping processes. We found that wood species also contributed to the differences in the formation of these volatile compounds in pulping.

ACKNOWLEDGEMENT

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Fig. 1

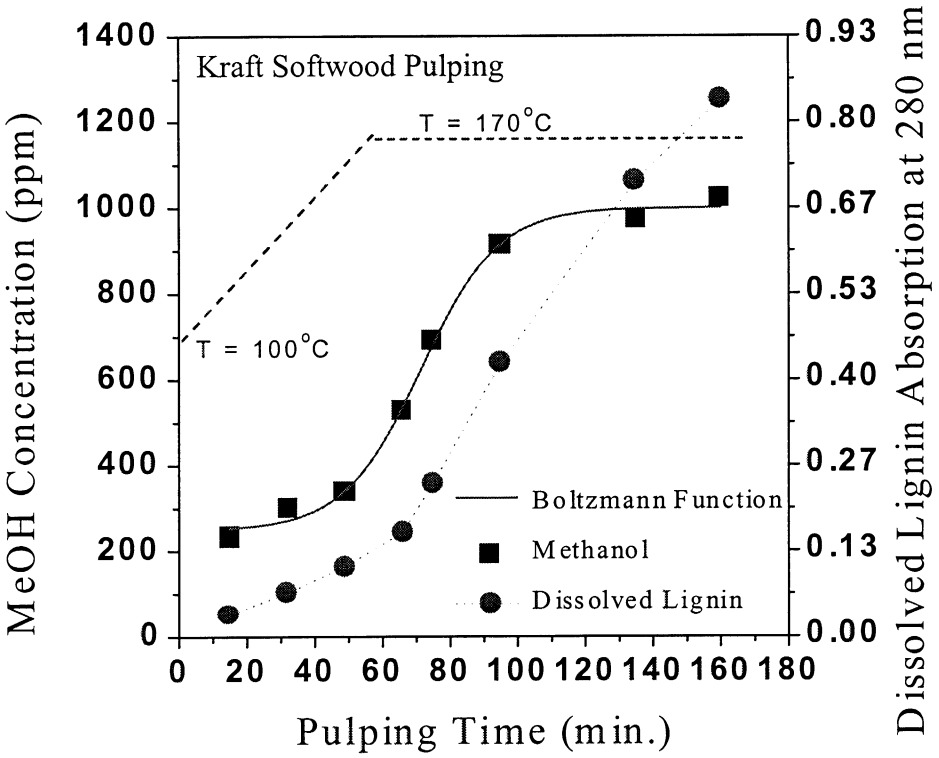
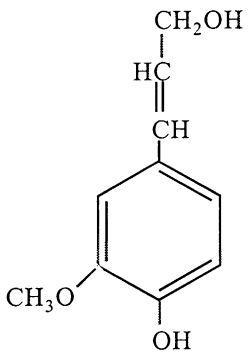
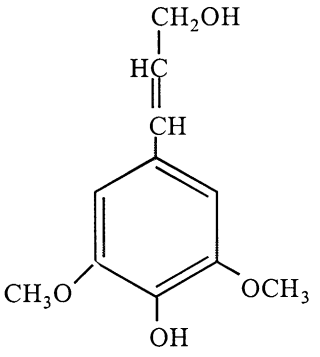


Fig. 2

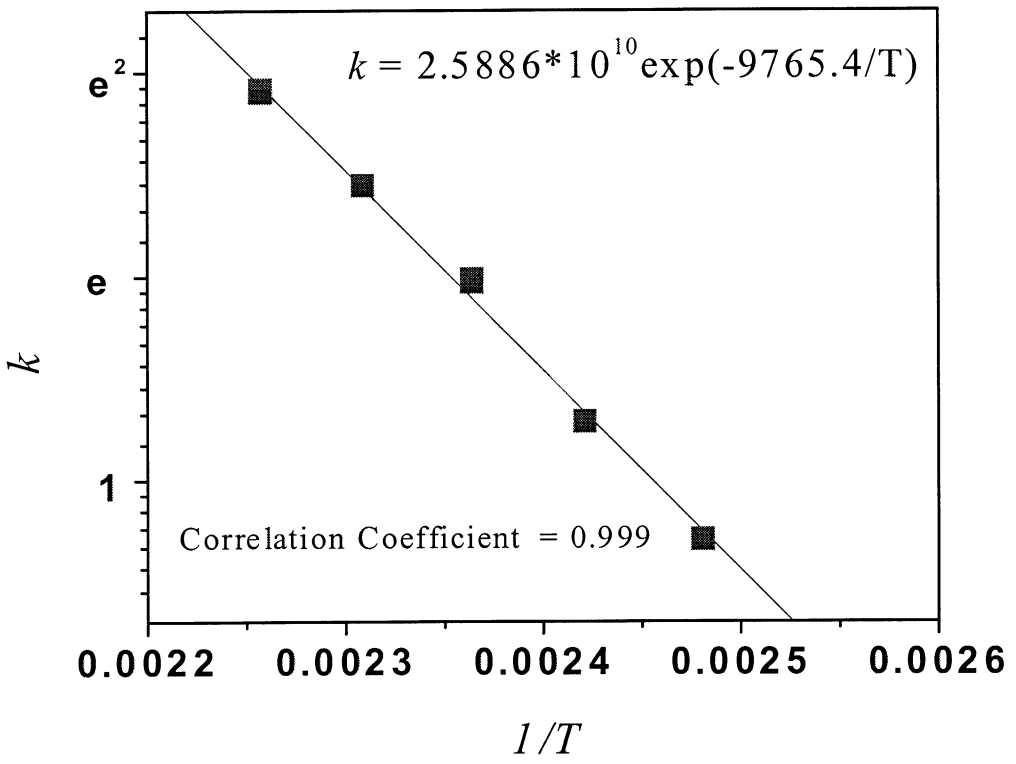


Coniferyl alcohol



Sinapyl alcohol

Fig. 3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e^2
e
1
k
Correlation Coefficient = 0.999
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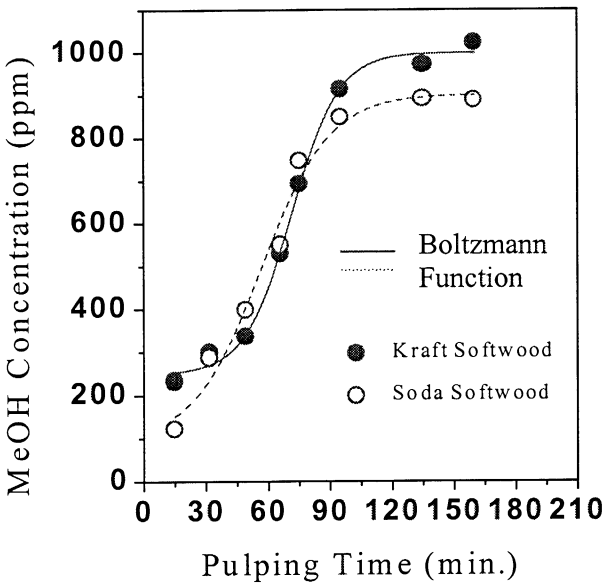
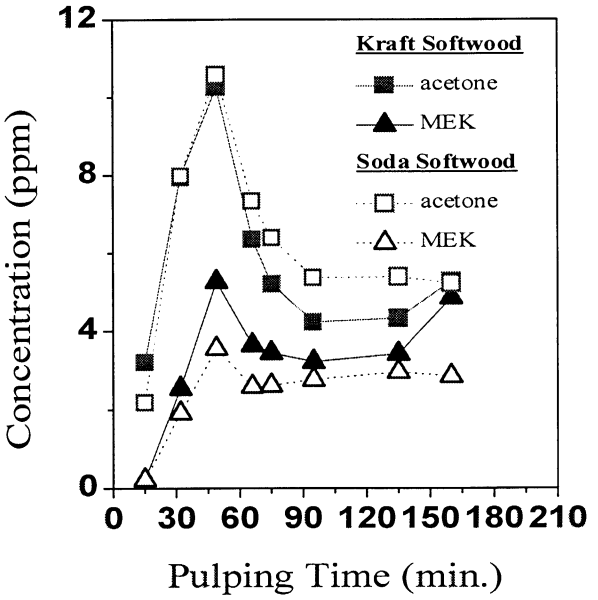
Fig. 4

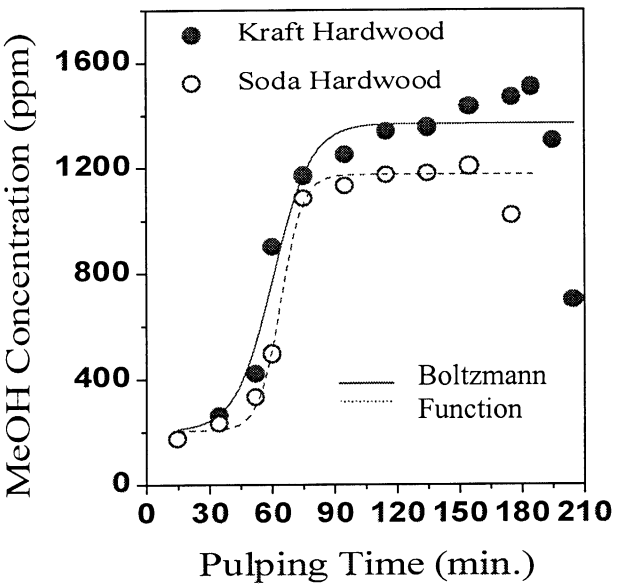


(a)

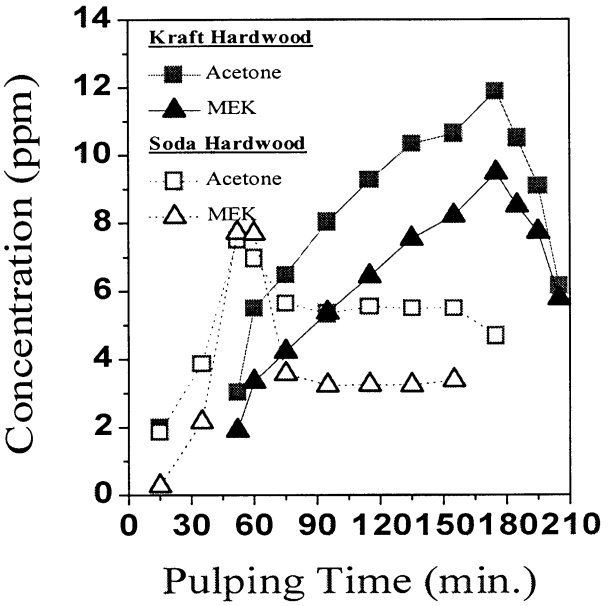


(b)

Fig. 5

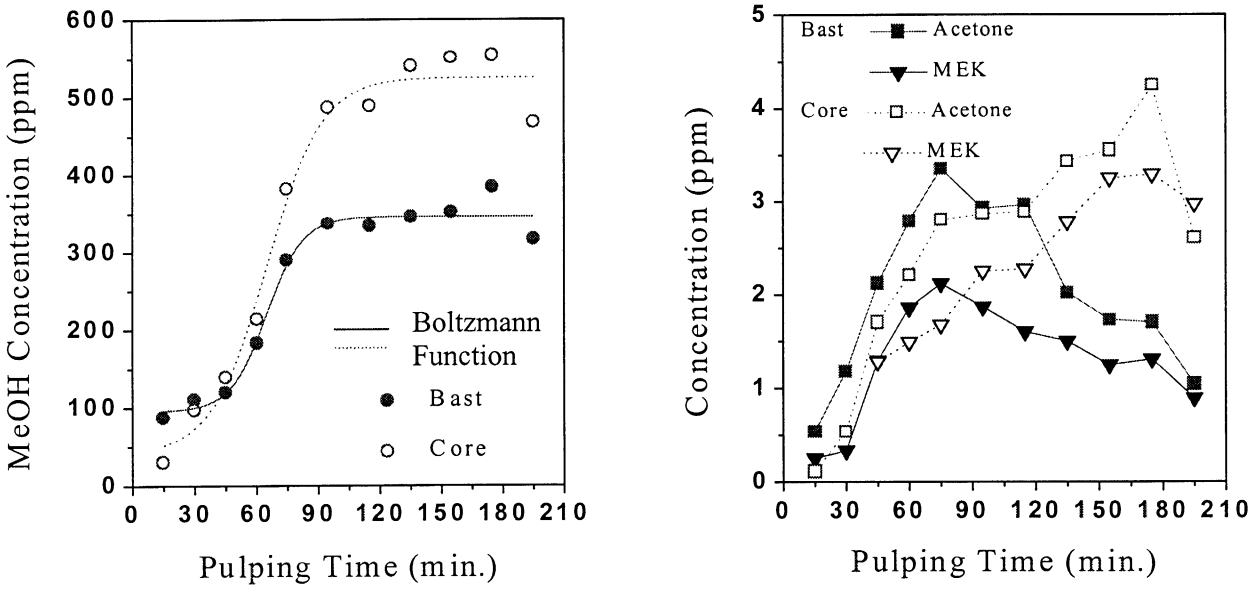


(a)



(b)

Fig. 6


MeOH Concentration (ppm)
600
500
400
300
200
100
0
0 30 60 90 120 150 180 210
Pulping Time (min.)
Boltzmann Function
Bast
Core
Concentration (ppm)
5
4
3
2
1
0
Bast
Acetone
MEK
Core
Acetone
MEK
0 30 60 90 120 150 180 210
Pulping Time (min.)

(a) **(b)**

Fig. 7

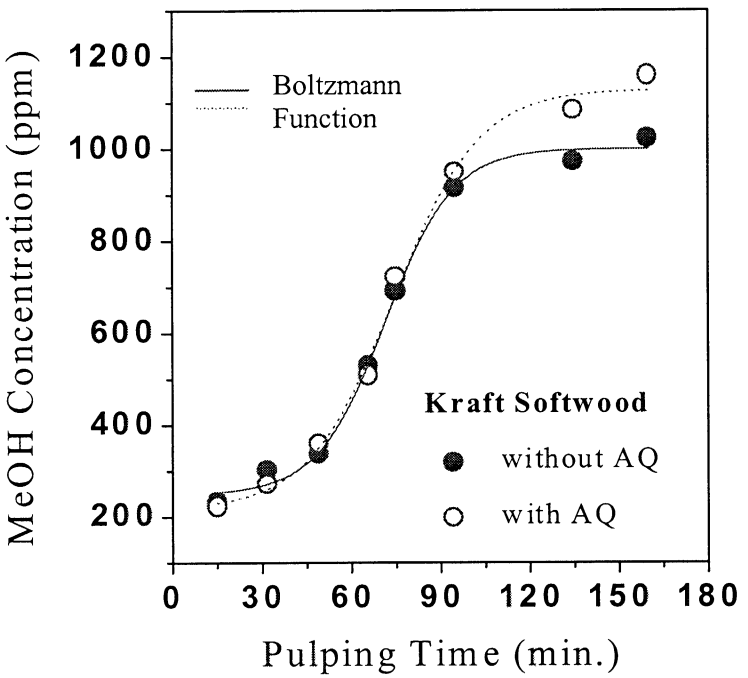

MeOH Concentration (ppm)
1200
1000
800
600
400
200
0 30 60 90 120 150 180
Pulping Time (min.)
Boltzmann Function
Kraft Softwood
without AQ
with AQ

Fig. 8

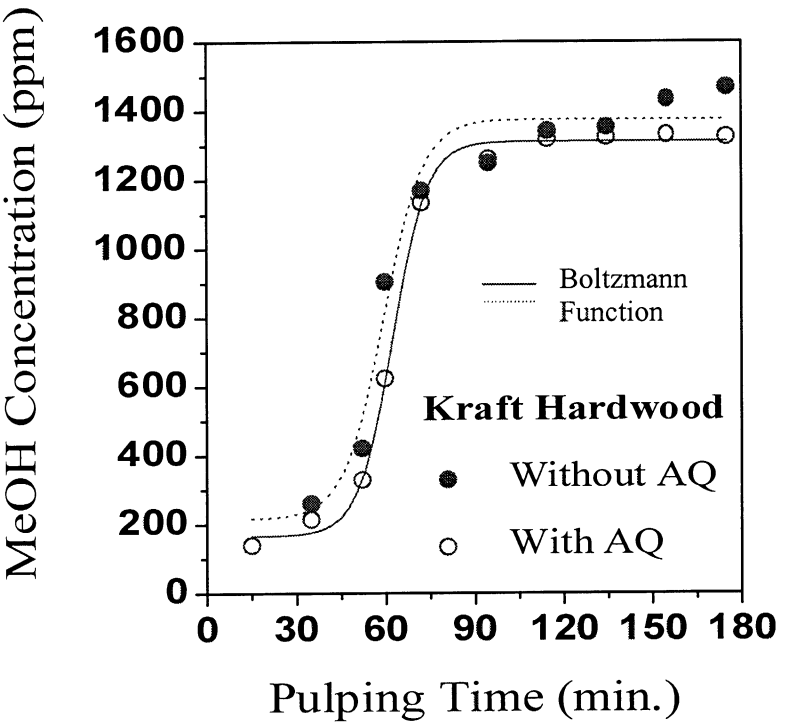


Table I: A list of pulping conditions

PARAMETERS	VALUES
Alkali (%)	18
Sulfidity (%)	0 for soda 25 for kraft
Liquid-to-Wood Ratio	4 for softwood and hardwood 8 for kenaf bast and core
Final Temperature (°C)	170
H Factor	2000
Catalyst	None and AQ for Woods AQ only for Kenaf

Table II: A list of final kappa numbers of the pulping processes

Pulping Material	Kappa Number	
	Kraft Pulping	**Soda Pulping**
Softwood	28 (with AQ) 31 (without AQ)	31 (with AQ) 34 (without AQ)
Hardwood	14 (with AQ) 14 (without AQ)	16 (with AQ) 25 (without AQ)
Kenaf: Bast	N/A	8 (with AQ)
Kenaf: Core	N/A	16 (with AQ)

Table III: Calculated methanol concentrations in the final cooking liquors of pine and birth based on 100% xylan demethylation.

Parameters	Birch	Pine
Xylan content (x_{xylan})	0.25	0.08
Ratio of xylose to 4-O-Methyl-Glucuronic Acid ($R_{megacid}$)*	10	3-6
Calculated methanol concentration due to Xylan Demethylation (mg/L)**	1041	740
Experimentally measured concentration in this study (mg/L)	1330	1020
Xylan demethylation contribution	78%	73%

* An average value, 4.5, was chosen in the calculation.

** The molecular weight of methanol and the 4-O-methyl-glucuronic acid of xylan are M_{MeOH} = 31 and $M_{megacid}$ =186, respectively. The liquid to wood ratio R_{LW} = 4.

Table IV: Calculated methanol concentrations in the final cooking liquors of pine and birth based on 2% lignin demethylation.

Parameters	Birch	Pine
Lignin Content (x_{lignin})	0.2	0.3
Ratio of lignin to coniferyl alcohol ($R_{conifalcoh}$)	0.62	1.0
Ratio of lignin to sinapyl alcohol ($R_{sinapalcoh}$)*	0.38	0
Lignin demethylated	0.02	0.015
Calculated methanol concentration due to Lignin Demethylation (mg/L)**	228	197
Experimentally measured concentration in this study (mg/L)	1330	1020
Lignin demethylation contribution	17%	19%

* The mole ratio of methanol to sinapyl alcohol of 2 in the reaction equation is used in the calculation.

** The molecular weight of methanol, coniferyl alcohol, and sinapyl alcohol are $M_{MeOH} = 31$, $M_{conifalcoh} = 177$, and $M_{sinapalcoh} = 198$, respectively. The liquid to wood ratio $R_{LW} = 4$.

Table V. Methanol mass balance

Parameters	Birch	Pine
Xylan Contribution (mg/L)	1041 (78%)	740 (73%)
Lignin Contribution (mg/L)	228 (17%)	197 (19%)
Total Calculated	1269 (95%)	937 (92%)
Experimentally Measured (mg/L)	1330	1020
Unaccounted (mg/L)	61 (5%)	83 (8%)